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A Semiannual Technical Report

from

Charles Evans and Associates
1670 South Amphlett Blvd. Suite #120
San Mateo, CA 94402

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Development and Application of SIMS Characterization
Techniques for the Study of Impurities and Impurity Motion in
(HgCd)Te and CdTe

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Principal Investigator Charles Evans, Jr.

Charles Evans, Jr., President
(415) 572-1601

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OBJECTIVES

The broad objectives of this program are (1) to develop quantitative analytical procedures for the application of high performance secondary ion mass spectrometry (SIMS) to the analysis of CdTe and (HgCd)Te for trace element and major constituent characterization, particularly Hg, and (2) to perform materials-directed research in order to better understand the incorporation and redistribution of impurity elements in CdTe and (HgCd)Te.

PROGRESS SUMMARY

A. Analytical Procedures

1. Standardization

The general problem of applying quantitative methods to secondary ion mass spectrometry (SIMS) has been reviewed by Werner.¹ Of the methods discussed, the relative sensitivity factor (RSF) approach has proved to be the most useful for the specific case of quantitative analysis of dopants and impurities in semiconductors by SIMS. For the RSF approach, standards are required. These are prepared by doping the material or matrix of interest with impurities in known concentrations and distributions. Relative sensitivity factors are simply multiplicative factors which relate ion intensity, as measured by SIMS for an impurity or dopant species, to concentration, for a given matrix. Their use is illustrated in the equation below:

$$[C_i] = \frac{I_i * RSF}{I_m} \quad (1)$$

where:

$[C_i]$ = concentration of impurity 'i' (atom/cm³)

I_i = instantaneous measured countrate of impurity 'i' (cts/sec)

I_m = instantaneous measured countrate of ¹²⁵Te (cts/sec)

Once the RSF for a dopant/matrix pair has been determined from a standard, it can be used to calculate the concentration of that dopant in other samples of the same matrix.

Ion implants into (HgCd)Te generally fulfill the requirements for SIMS standards. Therefore, under subcontract from CHARLES EVANS AND ASSOCIATES, Dr. Robert Wilson of Hughes Research Laboratories, Malibu, CA has prepared ion implants of many electropositive and electronegative elements into (HgCd)Te and CdTe. These ion implants have been depth profiled by SIMS and relative sensitivity factors derived by means of the relationship below:

$$RSF = \frac{D * \sum (I_m)}{d * \sum (I_i - (I_b + I_s))} \quad (2)$$

where:

d = analytical crater depth (cm)

D = implant fluence (atoms/cm²)

I_b = background countrate of impurity 'i' (cts/sec)

I_s = surface countrate of impurity ion 'i' (cts/sec)

The summations represent total counts over the measurement time.

Figure 1. shows a typical ion implant, illustrating the relationship of the variables from the equation above.

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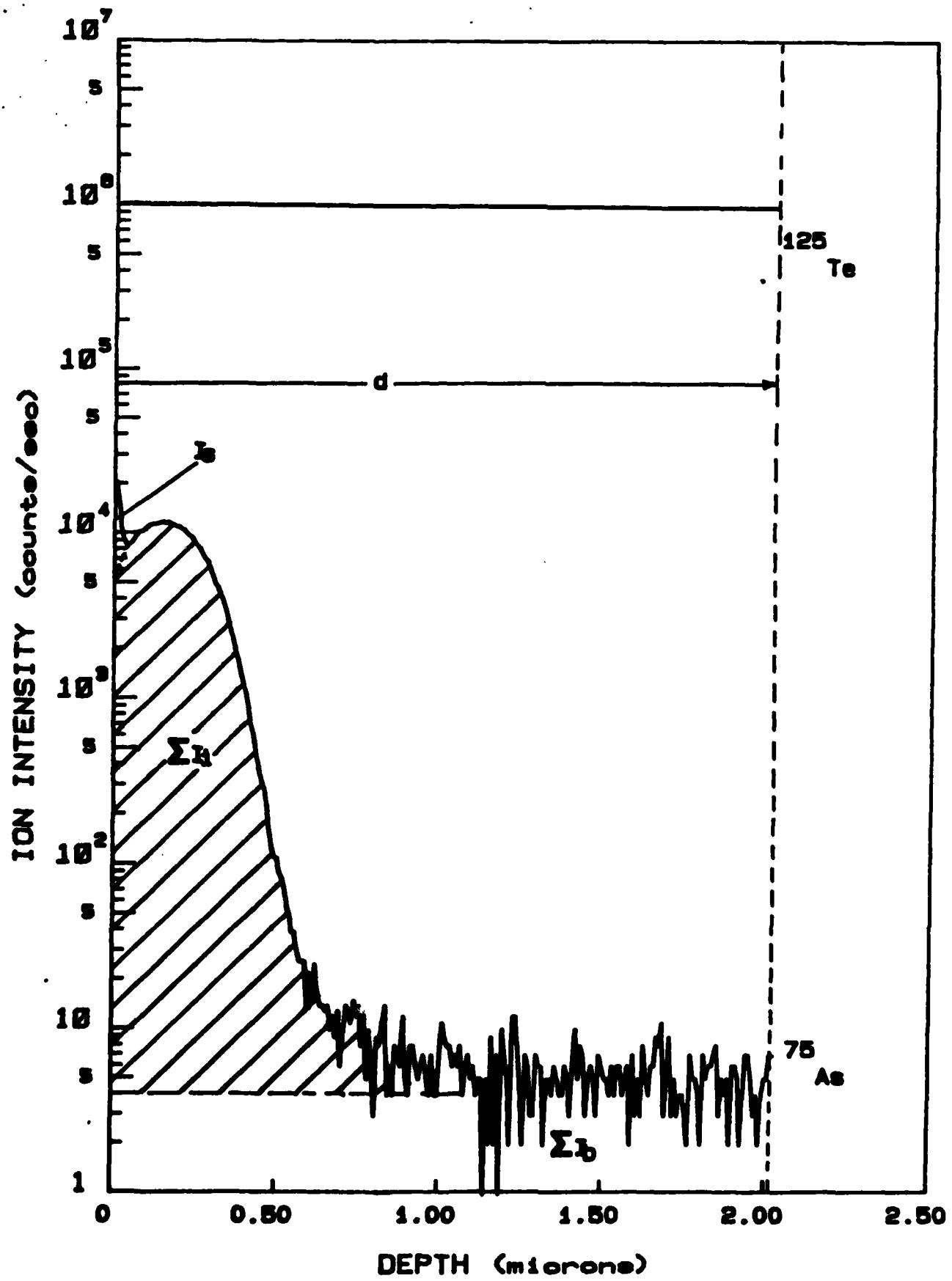


FIGURE 1. As IMPLANT INTO (HgCd)Te

The results of the RSF determinations are summarized below as Table A. The RSF's for electropositive elements (indicated below with a '+') were derived using O^+ bombardment SIMS. Cs^+ bombardment SIMS was used for the electronegative species (indicated below with a '-').

TABLE A. RELATIVE SENSITIVITY FACTORS FOR SELECTED ELEMENTS IN $(HgCd)Te$

<u>Element</u>	<u>Analyses</u>			
	<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>
Be^+	7×10^{19}			
B^+	1×10^{20}	2×10^{20}		
C^-	1×10^{22}			
O^-	2×10^{20}			
F^-	4×10^{19}	2×10^{19}		
Na^+	5×10^{16}	1×10^{17}	7×10^{16}	
Mg^+	2×10^{18}	1×10^{18}	7×10^{17}	9×10^{17}
Al^+	3×10^{17}	1×10^{17}		
Si^-	8×10^{22}	6×10^{22}		
P^-	1×10^{22}	2×10^{22}		
S^-	4×10^{20}			
Cl^-	3×10^{19}	8×10^{18}	6×10^{18}	8×10^{18}
Cu^+	4×10^{19}	8×10^{19}		
Ga^+	7×10^{17}	8×10^{17}		
As^-	3×10^{22}	2×10^{22}		
Br^-	1×10^{19}			
Se^-	8×10^{20}			
In^+	2×10^{17}	3×10^{17}	1×10^{17}	

Generally, the uncertainty in concentrations calculated using the RSF's as directly derived is estimated to be a factor of two. This is due in part to the spread of measured values for the RSF for a given element, as seen in the table above. This uncertainty is not a major drawback when measuring concentrations of elements present at parts-per million (ppma) levels or less in $(HgCd)Te$. However, sources of error in these measurements, both random and systematic should be discussed.

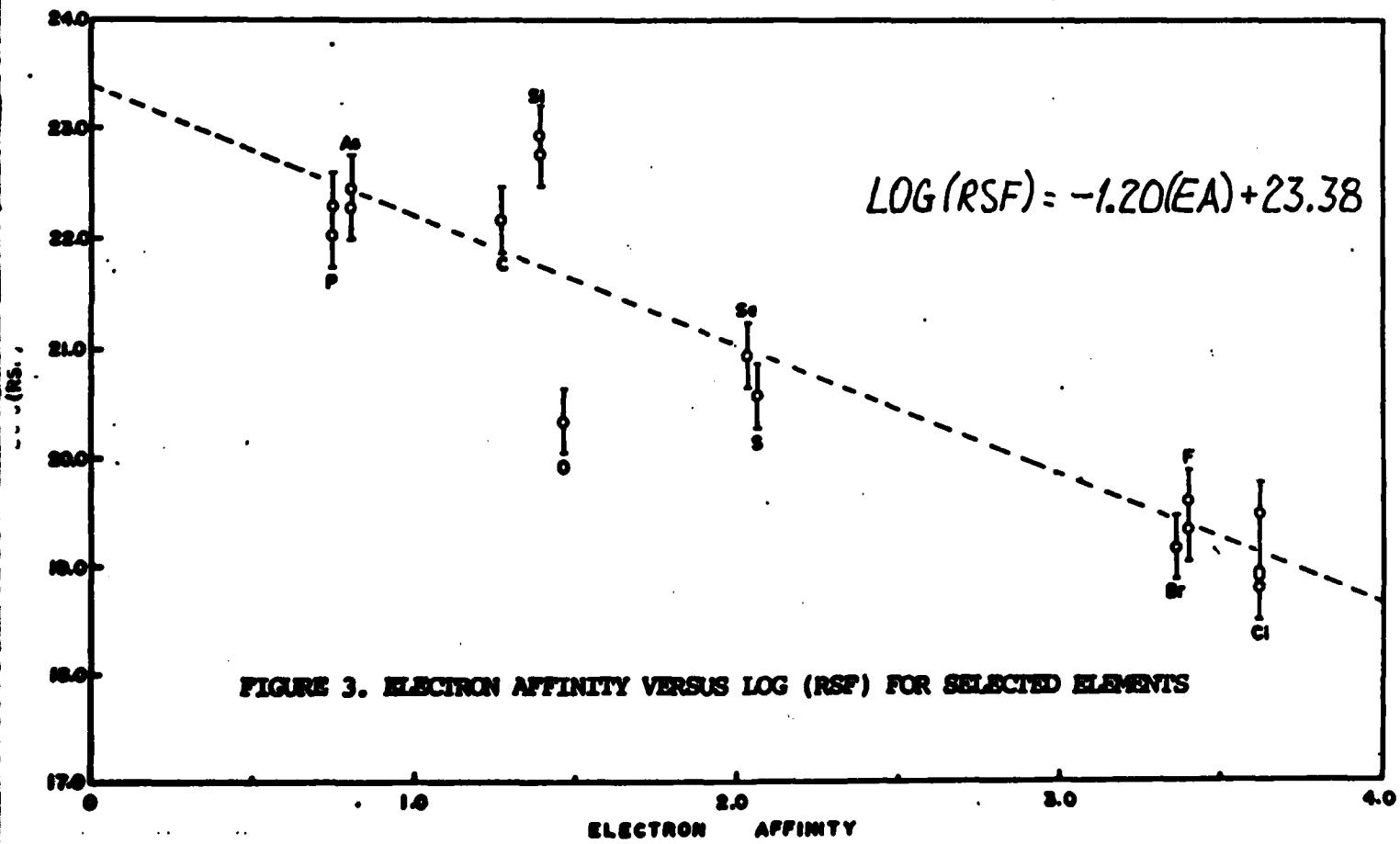
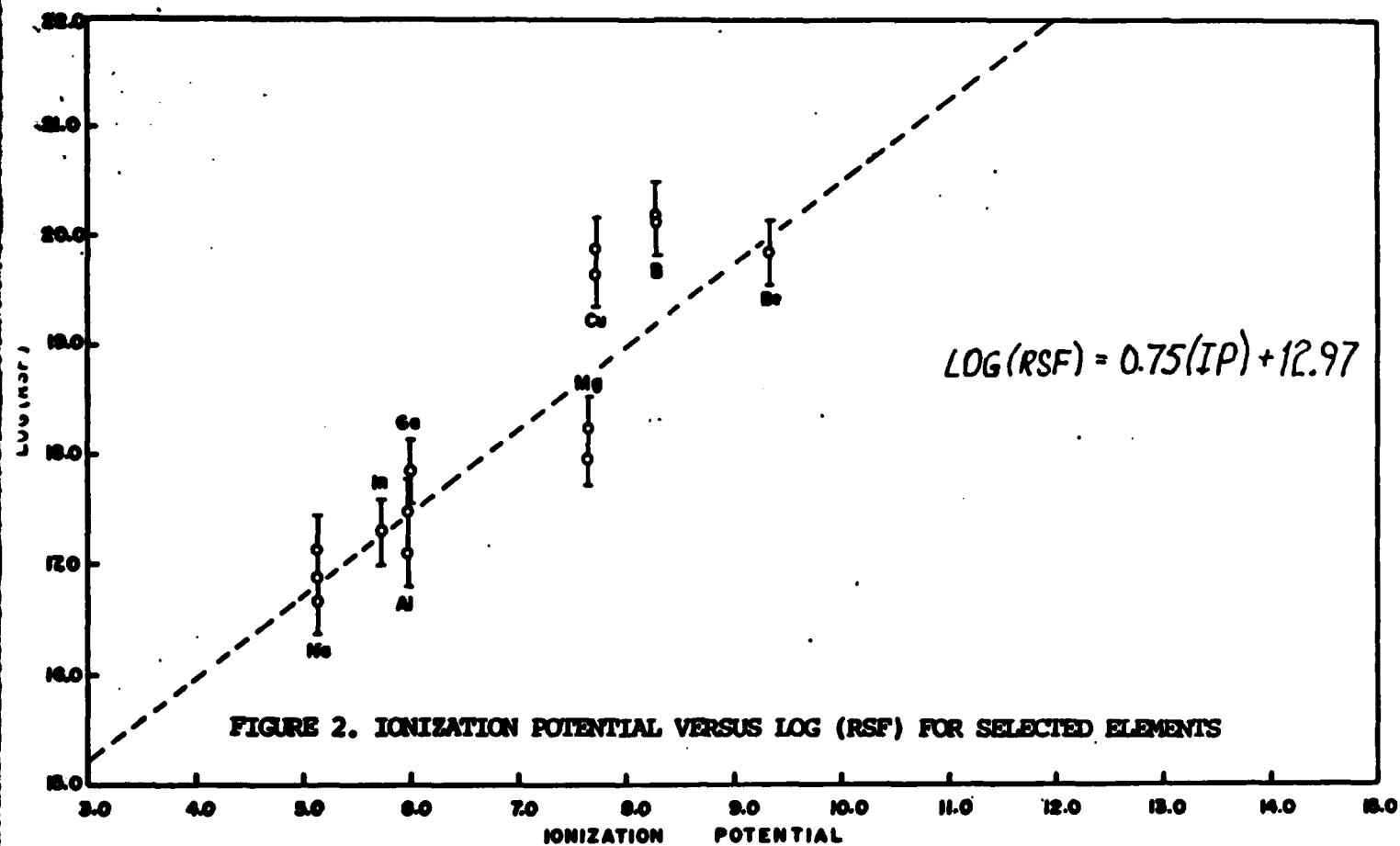
The precision or reproducibility of impurity ion intensity measurements relative to a matrix ion intensity by SIMS can be made better than 95% with particular attention to

analytical detail.² However, this precision is obtained only at great expense in terms of analysis time. This is compounded, in the case of (HgCd)Te, by the costs of acquiring the required amounts of uniformly implanted sample area, to compensate for the continuous consumption of the standards by SIMS analysis.

A source of systematic error is the inaccuracy of the fluence or dose measurement delivered by the dose integrator on the ion implanter. This error varies with dose and with the mass of both the ion being implanted and the average mass of the substrate and can be up to 35% of the implanted dose in (HgCd)Te.³ The effect in all cases is for the number of implanted atoms to be smaller than indicated.

Other effects on ion yield were considered. All the data presented were for (HgCd)Te with an atom fraction of Hg around 0.4. Initial studies done with ion implants of equivalent doses in both (HgCd)Te and CdTe indicate no observable differences in ion yield larger than the uncertainty of the data, except due to the surface charging of the CdTe. Thus, smaller changes in atom fraction of Hg should have a negligible effect on the RSF's.

The elements selected for implantation and subsequent SIMS analysis were picked for their potential utility as intentional dopants or unintentional impurities in (HgCd)Te.⁴ While it might be desirable to extend Table A to include most of the periodic table, this is neither practical nor cost effective. Accordingly, an attempt was made to systematize the data in Table A by means of a simple ion yield model, based loosely on the local thermal equilibrium (LTE) type, as proposed by Anderson and Hinckley.⁵ Our model presumes the sputtered ion yield of an element from CdTe and (HgCd)Te is influenced primarily by the first ionization potential or by the electron affinity of that element. Figure 2. is a plot of the common logarithm of the RSF for the electropositive elements versus ionization potential. Likewise, Figure 3. is a plot of the common logarithm of the RSF's for the electronegative elements versus electron affinity.



The least-squares fits to the data in Figures 2. and 3. agree well with data recently released from a similar, but proprietary internal research program at the Santa Barbara Research Center, Santa Barbara, CA.⁶ Note that while the fit of the electronegative species is within the uncertainty factor, the electropositive species fit is not good within the factor of two in uncertainty quoted for this data. Therefore, in calibrating the ion yields of electropositive species for which RSF's have been prepared, greater accuracy can be obtained by using the appropriate number from Table A. The curve is most useful at present to get an estimate of concentration for species which have not been prepared as ion implants.

B. Mass and Energy Spectra

At the beginning of this program we began a series of fundamental experiments on the initial kinetic energy distributions of the sputtered constituents from (HgCd)Te. Our work on this subject is a continuation of the results reported by Holland and Blackmore.⁷

Preliminary investigations indicated that the bulk of the Hg ions detected came from the space above the sample surface rather than the surface itself. This was a significant finding because it immediately led to a clearer understanding of Hg behavior under bombardment, and subsequently a more reproducible Hg analysis from (HgCd)Te.

A puzzling observation from the investigation of Hg ion yield in the above-surface region mentioned, was its apparent quadratic dependence on the flux of primary bombarding ions. Lack of a clear explanation for this lead to an investigation into the extent of the effect in other elements. Therefore, many more energy spectra were acquired during this reporting period in an attempt to shed light on the mechanism responsible for the quadratic dependence. The mechanisms we are presently examining involve the possibility that sputtering generates neutral atoms and clusters which are electronically excited. If this proves to be the case then theoretically it should be possible to induce these excited neutrals to ionize, thus increasing their detection efficiency, or sensitivity. Work is underway as of this writing to test this assumption.

C. Data Acquisition and Presentation

As previously mentioned, our ability to stay up to date on developments in analysis and growth of (HgCd)Te and related subjects has been tremendously improved by connection to the computerized data retrieval service DIALOG. This service, supplied by Lockheed

Aerospace, Sunnyvale, CA, allows on-line access to a very large number of machine-searchable citations abstracted from nearly every journal and text of importance. During this reporting period we have searched the relevant literature in preparation to study materials problems related to metal/(HgCd)Te bonds. These kinds of problems, common in the more mature device technologies of Si and GaAs are only now beginning to receive attention as potentially affecting device yield.

Some preliminary work has been done using Auger Electron Spectrometry, in combination with Energy Dispersive X-Ray analysis. These techniques have proved helpful in the past for analogous work on GaAs and Si. Also, we have begun to investigate the use of Laser Ion Mass Spectrometry on (HgCd)Te for rapid, very sensitive 'fingerprint' analysis. These analytical techniques will be the subject of a future report.

4. Significant Problems/Future Work

Work for the immediate future will concentrate on investigation of methods to increase ion yield from (HgCd)Te and reduce surface charging common to semi-insulating CdTe analyzed by SIMS.

More relative sensitivity factors will be determined as the remainder of the proposed ion implants are prepared and analyzed. These will be added to the results in Table A. as well as compared with the relationships indicated in Figures 2. and 3. Finally, consideration is being given to improvements in the simple ion yield model in order to match the observed data more closely.

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